भारतीय मानक
Indian Standard

IS 3025 (Part 29) : 2022

जल एवं अपशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियां

भाग 29 सलफाइड

(दूसरा पुनरीक्षण)

Methods of Sampling and Test (Physical and Chemical) for Water and WasteWater

Part 29 Sulphide

(Second Revision)

ICS 13.060.50

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भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुर शाह ज़फर मार्ग, नई दिल्ली - 110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002
www.bis.gov.in www.standardsbis.in

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Water Quality Sectional Committee, CHD 36

FOREWORD

‘This Indian Standard (Part 29) was adopted by the Bureau of Indian Standards, after the draft finalized by the Water Quality Sectional Committee had been approved by the Chemical Division Council’.

Sulphide is often present in ground water, especially in hot springs. Its common presence in waste waters comes partly from the decomposition of organic matter, sometimes from industrial wastes, but mostly from the bacterial reduction of sulphates. Hydrogen sulphide gas escaping in air from sulphide-containing waste waters cause odour nuisance. Hydrogen sulphide is a toxic gas. It attacks metals directly or indirectly.

The Technical Committee responsible for formulation of IS 2488 (Part 1) : 1966 ‘Methods of Sampling and test for Industrial Effluents — Part 1’ and IS 3025 : 1964 ‘Methods of Sampling and Test (Physical and Chemical) for water used in Industry’ decided to revise the standard and publish it in separate parts. This standard superseded **16** of IS 2488 (Part 1) : 1966 ‘Methods of Sampling and Test for Industrial Effluents — Part 1’ and **46** of IS 3025 : 1964 ‘Methods of Sampling and Test (Physical and Chemicals) for water used in Industry’ and was one among the different parts published under IS 3025 series of standards. The first revision of this standard was published in 1986.

In this second revision the following modifications have been incorporated:

a) Separation of soluble and insoluble sulphides and the pretreatment of sample to remove interfering substances (or to concentrate the sulphide) has been added; and

b) Iodometric method has been updated.

In the preparation of this standard, considerable assistance has been derived from the method no 4500 S^{2-} B,C, D, and F of Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 23rd Edition, 2017.

The composition of the committee responsible for the formulation of this standard is given at Annex A.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 ‘Rules for rounding off numerical values (*second revision*)’.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTE WATER

PART 29 SULPHIDE

(Second Revision)

1 SCOPE

This standard describes two following methods for the determination of total and dissolved sulphides in waters and waste waters:

a) Titrimetric iodine method or methylene blue method, based on the reaction of sulphide, ferric chloride and dimethyl-p-phenylenediamine to produce methylene blue. Ammonium phosphate is added after colour development to remove ferric chloride colour. The procedure is applicable at sulphide concentration between 2 and 20 mg/l; and

b) Iodometric method, is suitable for measurement of sulphide in concentration above 1 mg/l if interferences are absent and loss of hydrogen sulphide is avoided. The iodometric method is useful for standardizing the methylene blue colorimetric method and is suitable for analyzing samples freshly taken from wells or springs.

2 REFERENCES

IS No.	*Title*
17614 (Part 1) : 2021	Water quality — Sampling: Part 1 Guidance on the design of sampling programmes and sampling techniques
17614 (Part 3) : 2021	Water quality — Sampling: Part 3 Preservation and handling of water samples

3 SAMPLING AND STORAGE

3.1 Sampling and storage shall be done as prescribed in IS 17614 (Part 1) and IS 17614 (Part 3). Samples must be taken with a minimum of aeration and preserved at low temperature sulphide may be volatilized by aeration and any oxygen is advertently added to the sample may convert the sulphide to an unmeasurable form.

3.2 Preserve the sample with addition of 2 ml/l of zinc acetate. Samples not preserved must be analyzed immediately.

4 SEPARATION OF SOLUBLE AND INSOLUBLE SULPHIDES

Until the sample is completely free from suspended solids (dissolved sulphide equals total sulphide), in order to measure the dissolved sulphide, removal of insoluble matter is first required. This can be achieved by producing an aluminium hydroxide floc that is settled, leaving a clear supernatant for analysis.

4.1 Apparatus

4.1.1 *Glass Bottles with Stoppers*

Use 100 ml of glass bottles if the determination of sulphide is done by the methylene blue method and 500 to 1 000 ml if the determination is done by the iodometric method.

4.2 Reagents

4.2.1 *Sodium Hydroxide Solution*, 6N

4.2.2 *Aluminium Chloride Solution,* due to the hygroscopic and caking tendency of this chemical salt, purchase only 100 gm bottles of aluminium chloride hexahydrate. Dissolve the contents of a previously unopened 100 gm bottle in a volume of 144 ml distilled water.

4.3 Procedure

In a 100 ml glass bottle, add 0.2 ml of 6 N sodium hydroxide. Fill the bottle with sample and instantly add 4 drops (0.2 ml) aluminium chloride solution. Stopper bottle so that it has no air under stopper. Rotate to and fro about a transverse axis vigorously for 1 min or longer to flocculate the contents. Volume of the chemicals that are added is varied, in order to get good clarification without the use of large amounts and to produce a *p*H of 6 to 9. If a bottle with a quantity of 500 or 1 000 ml is used, add in proportion a larger amounts of reagents. Let the solution to settle until a clear supernatant can be withdrawn. This may take 5 to 15 min of time with proper flocculation. Do not wait than the required time. Either carry out analysis of the supernatant immediately or preserve it with 2 N zinc acetate.

5 SAMPLE PRE TREATMENT TO REMOVE INTERFERING SUBSTANCES OR TO CONCEMNTRATE THE SULPHIDE

The iodometric method experiences interference due to the reducing substances that can react with iodine, including sulphite, thiosulphate, and various other organic compounds, both solid and dissolved. Some strong reducing agents may interfere in the methylene blue method thereby preventing the formation of blue colour. Colour formation may be retarded or completely prevented by thiosulphate at concentrations of about 10 mg/l. Ferrocyanide gives a blue colour. The reaction is prevented by sulphide itself if its concentration is very high, in the range of several hundred milligrams per litre. In order to prevent the chance of false negative results, antimony method is used to obtain a qualitative result in industrial wastes which can possibly contain sulphide but does not show any colour by the methylene blue method. Iodide that is likely to be present in oil-field waste waters can diminish colour formation if its concentration exceeds 2 mg/l. Many metals (like Hg, Cd,Cu) form insoluble sulphides and provide low recoveries.

Eliminate the interferences which are due to iodide, sulphite, thio-sulphate and many other soluble substances, but not due to ferrocyanide, by first precipitating the zinc sulphide and then removing the supernatant and replacing it with distilled water. Use the similar procedure even when not required for removing the interferences, in order to concentrate sulphide.

5.1 Apparatus

5.1.1 *Glass Bottles with Stoppers*

5.2 Reagents

5.2.1 *Zinc Acetate Solution*

Dissolve of 220 gm of zinc acetate dehydrate in 870 ml water; then make the volume upto 1 l solution.

5.2.2 *Sodium Hydroxide Solution* (NaOH), 6 N

5.3 Procedure

5.3.1 Take 0.2 ml (4 drops) of zinc acetate solution and 0.1 ml (2 drops) of sodium hydroxide solution, 6 N in a 100 ml glass bottle, fill it with a sample and then add 0.1 ml (2 drops) of 6 N sodium hydroxide solution. Stopper it so that there are no air bubbles under stopper and mix it by vigorously rotating back and forth about a transverse axis. For an iodometric procedure, take a 500 ml bottle or other bottle of convenient size that can accommodate proportionally larger volumes of reagents. Vary the volume of reagents that are added according to the sample so that the precipitate formed is not bulky in excess and settles down quickly. Add sufficient amount of sodium hydroxide just to raise the *p*H above 9. Let the precipitate settle for 30 min. The sample that is treated is relatively stable and can be held for couple of hours. However, if iron is present in high concentration, oxidation may be little rapid.

5.3.2 In case iodometric method is used, collect the precipitate on a filter made of glass fibre and at once continue with the titration as per the iodometric method procedure. In case the methylene blue method is used, allow the precipitate to settle for 30 min and then decant maximum amount of supernatant without the loss of any precipitate. Refill the bottle with distilled water and shake it well to re-suspend the precipitate and then quickly withdraw a sample. If the interfering substances are present in high concentration, let them settle and decant and refill it for a second time. If the sulphide concentration is low, add only sufficient water to bring the volume upto one-half or one-fifth of original volume. Use the technique for analyzing samples of extremely low sulphide concentrations.

6 IODOMETRIC METHOD

6.1 Reagents

6.1.1 *Hydrochloric Acid (HCl)*, 6 N

6.1.2 *Standard Iodine Solution*, 0.025 N

Dissolve 20 to 25 gm of potassium iodide in a minimum amount of water and add 3.2 gm of iodine. After the dissolving iodine, dilute it to 1 000 ml and standardize it against 0.025 N sodium thiosulphate using starch solution as indicator.

6.1.3 *Standard Sodium Thio-Sulphate Solution*, 0.025 N

Dissolve 6.205 gm of sodium thiosulphate pentahydrate in reagent water. Add 1.5 ml of 6 M sodium hydroxide or 0.4 gm solid sodium hydroxide and dilute it to 1 000 ml with distilled water. Standardize the sodium thiosulphate solution by titrating it against potassium iodate solution.

6.1.4 *Starch Solution*

To prepare starch solution, either use the aqueous solution or soluble starch powder mixtures. For the preparation of aqueous solution, dissolve 2 gm laboratory grade soluble starch and 0.2 gm of salicylic acid (as a preservative) in about 100 ml of hot distilled water.

6.2 Procedure

6.2.1 Using a burette, measure into a 500 ml flask a sufficient amount of iodine solution (**6.1.2**) that is estimated to be an excess over the amount of sulphide present. Add distilled water if required, to bring the volume to about 20 ml. Add 2 ml of 6 N hydrochloric acid. Pipette out 200 ml of sample into a flask, by discharging the sample under solution surface. If the colour of the iodine disappears, additional amount of iodine is added till the colour remains. Carry out the back titration with sodium thiosulphate solution by adding a few drops of starch solution as end point is approached and continue till the blue colour disappears.

6.2.2 If sulphide was precipitated with zinc and zinc sulphide is filtered out, return the filter with precipitate to the original bottle and further add about 100 ml of water. Add iodine solution and Hydrochloric acid and titrate as in **6.2.1**.

6.3 Calculation

1 ml of 0.025 N iodine solution reacts with 0.4 mg S^{2-}:

Concentration of S^{2-}, $mg/l = \frac{(A \text{ x } B - C \text{ x } D) \text{ x } 16\,000}{V}$ ....(1)

where

A = Volume of iodine solution, in ml;

B = Normality of iodine solution;

C = Volume of $Na_2S_2O_3$ solution, in ml;

D = Normality of $Na_2S_2O_3$ solution; and

V = Volume of sample, in ml.

7 METHYLENE BLUE METHOD

7.1 Apparatus

7.1.1 *Matched Test Tubes,* with an outer diameter (OD) of approximately 15 mm and 125 mm long

7.1.2 *Droppers,* delivering the methylene blue solution (20 drops/ml). To obtain uniform drops keep the dropper in a vertical position and let the drops form gradually.

7.1.3 *Spectrophotometer,* suitable for use at a wavelength of 664 mm with cells providing the light paths of 1 cm and 1 mm or other path lengths or filter photometer, having a filter that provides a maximum transmittance near 660 nm.

7.2 Reagents

7.2.1 *Amine Sulphuric Acid Stock Solution*

Dissolve 27 gm of N, N-dimethyl-p-phenylene diamine-oxalate in cold 50 ml concentrated sulphuric acid and 20 ml of distilled water. Cool it and further dilute with a 100 ml distilled water. Make a use of fresh oxalate as an old stock may be oxidized and decolours to a degree that results in interfering colors in the test. Store it in a dark glass bottle. When the above stock solution is diluted and used in this procedure with a sulphide free sample, it will first turn pink but then it should become colourless just within 3 min.

7.2.2 *Amine-Sulphuric Acid Reagent*

Dilute about 25 ml of amine-sulphuric acid stock solution (*see* **7.2.1**) with 975 ml of diluted sulphuric acid (1:1). Store it in a dark glass bottle.

7.2.3 *Ferric Chloride Solution* ($FeC1_3.6H_2O$)

In 40 ml of distilled water, dissolve 100 gm of ferric chloride ($FeC1_3.6H_2O$).

7.2.4 *Sulphuric Acid Solution* (H_2SO_4), 1:1.

7.2.5 *Diammonium Hydrogen Phosphate Solution* [$(NH_4)_2HPO_4$]

To 800 ml of distilled water dissolve 400 g of diammonium phosphate [$(NH_4)_2HPO_4$].

7.2.6 *Methylene Blue Solution I*

Dissolve about 1.0 gm of dye (should be 84 percent or more) in distilled water and make up the volume upto 1 l. This solution will approximately be of the correct strength but due to the variation between the dyes of different lots, standardize it against sulphide solutions strength of which is known and adjust its concentration in such a way that it contains 0.05 ml (1 drop) = 1.0 mg of sulphide/l. The procedure for standardization is given below:

7.2.7 *Standardization of the Solution*

Prepare about five known concentrations of sulphide standards that ranges from 1 to 8 mg/l as follows:

7.2.7.1 Put few grams of clean, washed crystals of sodium sulphide nanohydrate [$Na_2S.9H_2O$] into a small beaker. Add water in amount just to cover the crystals. Stir the solution occasionally for sometime (few minutes) and then pour it in another vessel. This solution will react with oxygen at a slow speed but the change can be insignificant if the analysis is performed within a few hours. Prepare the solution on daily basis. To a 1 l of distilled water, add 1 drop of sodium sulphide solution and mix. Immediately determine the concentration of sulphide by methylene blue procedure or by iodometric procedure. Repeat using more than 1 drop of sodium sulphide solution or water in small volumes till minimum of five tests have been made with a sulphide concentration in the range of 1 and 8 mg/l.

7.2.8 *Methylene blue solution II*

Dilute about 10 ml of adjusted methylene blue solution I to 100 ml by adding distilled water to it.

7.3 Procedure

7.3.1 *Colour Development*

Transfer 7.5 ml of the sample in each of two matched test tubes. In case the sample has been preserved by using zinc acetate, shake it vigorously before taking its sub-sample. To Tube A, add about 0.5 ml of amine-sulphuric acid reagent and 0.15 ml (3 drops) of ferric chloride solution. Mix it immediately by slowly inverting it, only once. To Tube B, add about 0.5 ml 1:1 sulphuric acid and 0.15 ml (3 drops) of ferric chloride solution and mix. The sulphide (S^{2-}) presence will be indicated by the blue colour in Tube A. Development of colour is usually complete in about 1 min but a longer time is generally required for fading out the pink colour that developed initially. Wait for about 3 to 5 min and then add 1.6 ml of diammonium phosphate solution to each test tube. Wait for the time period of 3 to 15 min and make the comparisons between the colour. In case zinc acetate was used, wait for a minimum of 10 min before making a visual comparison between the colour.

7.3.2 *Colour Determination*

7.3.2.1 *Visual Colour Estimation*

Add methylene blue solution I or II, depending on the concentration of sulphide and accuracy as desired drop by drop to the second tube till the colour matches to that developed in the first tube. In case the concentration exceeds to 20 mg/l, repeat the entire test with a portion of sample that is diluted to ten – fold. The methylene blue solution I is so adjusted such that 0.05 ml (1 drop) is equivalent to 1.0 mg S^{2-}/l when 7.5 ml of sample are used:

Concentration of S^{2-}, mg/l

= no. of drops of solution I + 0.1 (no. of drops of solution II)

7.3.2.2 *Photometric Colour Measurement*

A cell with 1 cm of light path of is suitable for measuring the concentrations of sulphide from 0.1 to 2.0 mg/l. Shorter or longer light paths may be used for high or low concentrations. The method is suitable for concentration of sample up to 20 mg/l. Set zero on the instrument with a part of treated sample from Tube B. Prepare the calibration curves on the basis of the colorimetric tests made on sodium sulphide solutions which are simultaneously analyzed by the iodometric method, by plotting concentration versus absorbance. Linear relationship between absorbance and concentration can be estimated from 0 to 1.0 mg/l. Read the concentration of sulphide from calibration curve.

ANNEX A

(*Foreword*)

COMMITTEE COMPOSITION

Water Quality Sectional Committee, CHD 36

Organization(s)	*Representative(s)*
Chief Scientist, EPTRI, Hyderabad	SHRI N. RAVEENDHAR (***Chairman***)
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Environment Protection and Training Research Institute, Hyderabad	DR J. S. SRINIVAS
FAD 14,	MEMBER SECRETARY
Gujarat Pollution Control Board, Gandhinagar	DR D. N. VANSADIA SHRI K. B. VAGHELA (*Alternate*)
In Personal Capacity *(1221, Mahatma Gandhi Road, P. O. - Haridevpur, Kolkata, 700082)*	SHRI SANJIB KUMAR GOSWAMI
In Personal Capacity	SHRI. RAKESH MALHOTRA
In Personal Capacity, Hyderabad	SHRI N. MURALI MOHAN

Organization(s)	*Representative(s)*
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MS SHUBHANJALI UMRAO

Scientist ‘B’ (CHD), BIS

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BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones: 2323 0131, 2323 3375, 2323 9402 *Website*: www.bis.gov.in

Regional Offices:		*Telephones*
Central	: 601/A, Konnectus Tower -1, 6th Floor, DMRC Building, Bhavbhuti Marg, New Delhi 110002	2323 7617
Eastern	: 8th Floor, Plot No 7/7 & 7/8, CP Block, Sector V, Salt Lake, Kolkata, West Bengal 700091	2367 0012 2320 9474
Northern	: Plot No. 4-A, Sector 27-B, Madhya Marg, Chandigarh 160019	265 9930
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Western	: Plot No. E-9, Road No.-8, MIDC, Andheri (East), Mumbai 400093	2821 8093

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